

The Effect of Surfactant “2-[(3-Dodecanamidopropyl)dimethylaminio] Acetate” on Structural Properties of Polyacrylonitrile Copolymer

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Abstract Hydrodynamic properties of polyacrylonitrile (PAN) in *N,N*-dimethylformamide (DMF) medium were studied in the presence and absence of amphoteric surfactant “2-[(3-Dodecanamidopropyl)dimethylaminio] acetate” known as betaine, through changes in a viscosity and specific electrical conductivity. The critical micelle concentration of betaine is determined by specific electrical conductivity. Thermodynamic functions of micelle formation of betaine are studied. Reduced viscosity of PAN copolymer in DMF is studied at different temperatures; it is found that temperature change does not affect the mechanism of a crystalline structure formation of PAN solutions. The reduced viscosity of PAN solution in the presence of betaine decreases 40 % on average at high concentrations. Hydrodynamic volume of PAN macromolecules decreases in the presence of betaine. The hydrogen bonding formation between the carbonyl groups of acrylamide in PAN copolymer and the amide groups in betaine is identified by FT/IR spectra. Crystalline structure of PAN in the presence of betaine and its absence is studied by X-ray diffraction and scanning electron microscopy.

Keywords Polyacrylonitrile · Viscosity · Fiber · Spinning · Mechanical and structural properties · Surfactants

1 Introduction

Resins of PAN are made from mixtures of monomers with acrylonitrile as the main component. It is a versatile polymer

which is used to produce large variety of products including ultra filtration membranes, hollow fibers for reverse osmosis, fibers for textiles, and oxidized PAN fibers. PAN fibers are the chemical precursor of high-quality carbon fiber [1–5]. It is found that electrospinning of PAN solutions at higher temperatures produces fibers with less crystalline but the chain orientation is higher. However, the activation energy of viscous flow increases with PAN concentration [6].

Branched PAN is prepared through self-condensing atom transfer radical copolymerization of acrylonitrile and 2-(2-bromopropionyloxy) ethyl acrylate which has obviously low intrinsic viscosity compared with its linear analogue. This property can be important for the spinning process in the production of acrylic fibers [7].

Mechanical and structural properties are considered the most important properties in the study of polymeric structure. Getting polymers with mechanical and structural properties in advance depends on the so-called structural modification orientations. This can be obtained if we have a simple change in the polymeric composition or by adding some low molecular mass materials such as surfactants to the polymeric solution. Unfortunately, studies on the effect of these materials on the structural properties of the polymer systems are almost rare and sporadic [8–15].

The effect of surfactants depends on the selectivity of adsorption at the interface between amorphous and crystalline regions of the polymer. In this case, the properties of the surfactants of the introduced doping agents are very important. The effects of different surfactants on hydrodynamic characteristics of PAN in DMF are studied. It is demonstrated that additives cause decrease of intrinsic viscosity and this is due to contraction of the macromolecular coil [16].

The purpose of this study was to lay the foundations of the formation of PAN structure in the presence of betaine.

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2 Experimental

2.1 Materials

2.1.1 polyacrylonitrile

Industrial fibers of PAN with a molecular weight 100,000 g/mol, glass transition temperature 98 °C and fusion 320 °C containing the following monomers: acrylonitrile $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ (85 wt%), acrylamide $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$ (11 wt%) and vinylacetate (4 wt%) $\text{CH}_2=\text{CH}-\text{O}-\text{CO}-\text{CH}_3$ (Adnan Shabarec Co.).

2.1.2 *N, N*-dimethylformamide

DMF solvent, pH value 7, purity (GC) $\geq 99.5\%$ (MERCK Co.).

2.1.3 Surfactant

2-[(3-Dodecanamidopropyl)dimethylaminio] acetate “C₁₉H₃₈N₂O₃” known as betaine is used as amphoteric surfactant (Shanghai Oli Enterprised Co.).

2.2 Instruments

2.2.1 X-ray Diffractometer

The XRD patterns of PAN are obtained using a STOE transmission STADI diffractometer, with copper as target and nickel as filter ($\lambda = 1.5408 \text{ \AA}$) at 30 kV and 30 mA. The scanning speed is 3.7 min^{-1} in the range $2\theta = 10\text{--}90^\circ$ at 298 K.

2.2.2 Scanning Electron Microscope

Morphologies of PAN samples are studied from the cryogenically fractured surface, sputtered with gold before viewing under a SEM (TESKAN VECA II) with accelerating voltage of 10 kV.

2.2.3 Falling Ball Viscometer

The falling ball viscometer (HAAKE Co.) corresponds to the requirements of many international standards (ISO 12058 and the German standard DIN 53015). The measuring tube is jacketed by means of an outer glass tube to control the solution temperature ($\pm 0.03^\circ\text{C}$ for test temperatures between 10 up to 80°C). This device can measure the viscosity ranging between 0.3 and 75,000 mPa s. Every value is measured three times and then averaged.

2.2.4 Ubbelohde Viscometer

Viscosity measurements of the dilute solutions of PAN 1–7.5 g/L are made in a thermostatic transparent water bath at $25 \pm 0.1^\circ\text{C}$ using an Ubbelohde viscometer which corresponds to the requirements of the international standard (ISO 3104). Every value is measured three times and then averaged.

2.2.5 Conductometer

Specific electrical conductivity is measured by SANXIN-MP 513 Lab Conductivity Meter.

2.2.6 FT/IR Spectrometer

FT/IR-4200 type A with a wave number range $4000\text{--}400 \text{ cm}^{-1}$ and an accuracy ($\pm 4 \text{ cm}^{-1}$) is used to investigate the structural changes.

2.3 Preparation of PAN Solutions

The PAN solutions are prepared in range 1–100 g/L, where PAN fibers are dissolved in DMF by continuous stirring at laboratory temperature, and then transparent polymeric solutions are obtained. Also, PAN solutions are prepared in the presence of betaine. Then, hydrodynamic properties of these preparative solutions are studied.

2.4 Preparation of PAN Solid Samples

The solid samples of PAN are prepared in order to study their crystalline structure in the following way. PAN solutions are prepared in the presence and absence of surfactant, and then poured in Petri dishes, put in dryer at 50°C until the complete vaporization of DMF, where solid samples are obtained; and these samples are examined by XRD and SEM.

3 Results and Discussion

Data about the micelle formation in organic mediums are very scarce and fragmentary. It is necessary to note here that there is a difference between micelle formation in organic mediums and water. The operations of micelle formation in water are organized by a hydrophobic influence of surfactant, while operations in an organic medium are organized by an enthalpy value of micelle formation [8].

The CMC of betaine in DMF medium is determined by a specific electrical conductivity (SEC) at different temperatures. The logarithm of SEC versus concentration of betaine plots shows a break at a concentration corresponding to the CMC [17]. Values of CMC are listed in Table 1.

Table 1 Values of CMC of betaine at different temperatures

<i>T</i> (K)	CMC (mol/L)
293	0.019
298	0.021
303	0.023

Table 2 Values of thermodynamic functions of micelle formation at 298 K

$-\Delta G$ kJ/mol	$-\Delta S \times 10^2$ kJ/mol K	$-\Delta H$ kJ/mol
9.819	1.6	14.569

The effect of temperature on micelle formation is investigated through the following Arrhenius equation:

$$\text{CMC} = A \exp \Delta H_m^\circ / RT \quad (1)$$

ΔH_m° : enthalpy of micelle formation; *A*: constant related to the nature of the solution; *R*: universal gas constant *T*: absolute temperature.

Equation (1) can be expressed in the logarithm form as:

$$\log \text{CMC} = \log A + \frac{\Delta H_m^\circ}{2.303R} \frac{1}{T} \quad (2)$$

The plot of log CMC against $1/T$ yields a straight line, the slope of which gives (ΔH_m°) . Then, Gibbs energy (ΔG_m°) and Entropy (ΔS_m°) of micelle formation are determined by the following equations at 298 K, respectively [8, 18]:

$$\Delta G_m^\circ = 2.303RT \log \text{CMC} \quad (3)$$

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ - \Delta G_m^\circ}{T} \quad (4)$$

Values of thermodynamic functions are listed in Table 2.

Table 2 shows that $\Delta G_m^\circ < 0$ this is compatible with the fact that operation of micelle formation is spontaneous, $\Delta S_m^\circ < 0$ this is due to the fact that the system becomes more regular when micelle formation. We also find that the leading force for the process of micelle formation can be considered a large value of ΔH_m° [19, 20].

It should be mentioned here that amphoteric surfactants act as a nonionic surfactant in the field of pH = 4–9 [21].

Viscosity (η) of PAN concentrated solutions 10–100 g/L is measured at 298, 308, 318, 328 K which is estimated through the following equation:

$$\eta = E(d_1 - d_2)t \quad (5)$$

E: ball constant; d_1 : ball density; d_2 : solution density; *t*: falling time of the ball.

Then, each of a specific viscosity (η_{sp}) and a reduced viscosity (η_{red}) are calculated through the following equations [9]:

Table 3 Density (*d*) of PAN solutions at 298 K

Solution	<i>d</i> (g/cm ³)
DMF	0.923
PAN 1 g/L	0.927
PAN 2.5 g/L	0.931
PAN 5 g/L	0.934
PAN 7.5 g/L	0.935
PAN 10 g/L	0.936
PAN 20 g/L	0.940
PAN 30 g/L	0.942
PAN 40 g/L	0.945
PAN 60 g/L	0.949
PAN 80 g/L	0.954
PAN 100 g/L	0.958

Table 4 Viscosity of PAN solutions

<i>T</i> (K)	PAN concentration <i>C</i> (g/L)							
	PAN viscosity η (mPa s)							
	0	10	20	30	40	60	80	100
298	0.473	1.495	3.210	8.831	15.813	46.338	109.333	264.968
308	0.420	1.221	2.751	7.359	12.876	37.971	90.210	224.973
318	0.375	1.097	2.293	6.227	10.843	30.892	70.102	164.980
328	0.339	0.955	2.030	5.321	9.261	25.743	56.234	129.980

Table 5 Reduced viscosity of PAN solutions

<i>T</i> (K)	PAN concentration <i>C</i> (g/L)							
	Reduced viscosity η_{red} (L/g)							
	10	20	30	40	60	80	100	
298	0.216	0.289	0.589	0.81	1.616	2.876	5.591	
308	0.19	0.277	0.55	0.71	1.49	2.672	5.346	
318	0.192	0.255	0.52	0.697	1.356	2.324	4.389	
328	0.181	0.249	0.489	0.657	1.248	2.061	3.824	

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \quad (6)$$

$$\eta_{red} = \frac{\eta_{sp}}{C} \quad (7)$$

η_0 : solvent viscosity; *C*: concentration of PAN solutions.

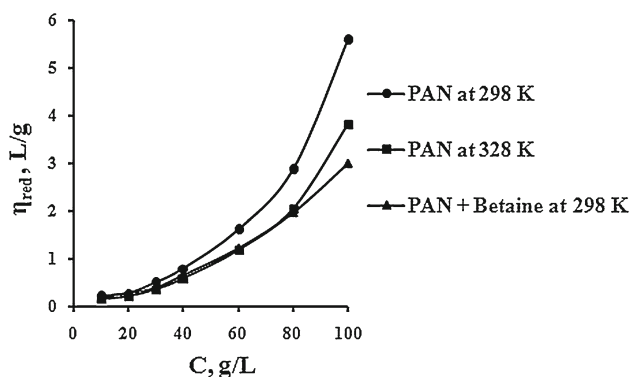
The results are listed in Tables 3, 4 and 5.

We will focus in our research on the study of the effect of betaine micelle on the structural properties of PAN. For this purpose, we have chosen the concentration of betaine 0.075 mol/L, which indicates the inevitability of micelle formation (see Table 1), as well as the presence of betaine molecules in solution freely.



Table 6 Viscosity and reduced viscosity of PAN solutions in the presence of 0.075 mol/L of betaine at 298 K

Solution	PAN concentration C (g/L)						
	10	20	30	40	60	80	100
η (mPa s)	1.355	3.199	8.122	13.121	35.542	75.313	136.334
η_{red} (L/g)	0.186	0.288	0.539	0.668	1.235	1.977	2.872

**Fig. 1** Reduced viscosity dependence on PAN concentration in the presence of 0.075 mol/L of betaine and its absence

Values of the viscosity and reduced viscosity of PAN solutions in the presence of 0.075 mol/L of betaine at 298 K are listed in Table 6.

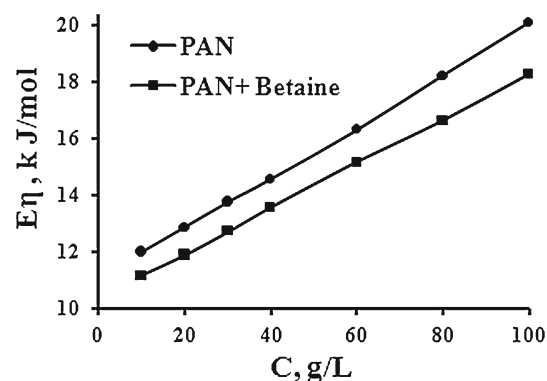
Figure 1 shows the reduced viscosity dependence on PAN concentration at 298, 328 K and in the presence of betaine at 298 K.

Figure 1 shows that nonlinear relationship linking the η_{red} with concentration. η_{red} markedly increases at the percolation threshold of a crystalline structural formation (50 g/L approximately). This refers to the interaction between dipoles of PAN which leads to the occurrence of strong associations of macromolecules. Figure 1 also shows that temperature change does not affect the mechanism of a crystalline structure formation. From Fig. 1, we find that the η_{red} of PAN solutions in the presence of betaine decreases 40 % on average at high concentrations. This is due to the influence of betaine and micelle formation on conformation of PAN molecules, which weakens the intermolecular interaction between PAN molecules. In addition, the presence of betaine surfactant in the PAN solutions does not lead to change in the percolation threshold of a crystalline structural formation [8–15, 22].

We can study the effect of temperature on viscosity of PAN solutions in the presence of betaine and its absence by using Arrhenius equation which can be written in the logarithm form as:

$$\log \eta = \log A + \frac{E_{\eta}}{2.303R} \frac{1}{T} \quad (8)$$

E_{η} : activation energy of viscous flow.

**Fig. 2** E_{η} dependence on PAN concentration in the presence of 0.075 mol/L of betaine and its absence**Table 7** Viscosity and reduced viscosity of dilute solutions of PAN in the presence of 0.075 mol/L of betaine and its absence

PAN concentration C (g/L)	Viscosity η (mPa s)		Reduced viscosity η_{red} (L/g)	
	PAN	PAN + betaine	PAN	PAN + betaine
1.0	0.533	0.530	0.127	0.121
2.5	0.637	0.625	0.139	0.129
5.0	0.851	0.813	0.160	0.144
7.5	1.115	1.033	0.181	0.158

The plot of $\log \eta$ against $1/T$ yields a straight line, from a slope of a straight line calculate the E_{η} .

Figure 2 shows the relationship between E_{η} and PAN concentration in the presence of 0.075 mol/L of betaine and its absence.

Figure 2 shows that the E_{η} of PAN solutions in the presence of betaine decreases 7 % approximately, this can be attributed to the fact that betaine weakens the intermolecular interaction between PAN molecules [6, 8].

Values of the viscosity and reduced viscosity of dilute solutions of PAN 1–7.5 g/L in the presence 0.075 mol/L of betaine and its absence, at 298 K, are listed in Table 7.

Figure 3 shows the relationship between reduced viscosity and concentration of the dilute solutions of PAN in the presence and absence of betaine to determine an intrinsic viscosity ($[\eta]$) at 298 K.

Figure 3 shows that $[\eta]$ is a point of intersection of the straight line with the axis η_{red} . The interaction between the polymer molecules diminishes significantly at this point. The value of $[\eta]$ of PAN solutions was equal to 0.118 L/g, while $[\eta]$ was equal to 0.115 L/g in the presence of betaine. Decrease in the value of $[\eta]$ in the presence of betaine surfactant is due to the decrease in the hydrodynamic volume of macromolecules [10, 16].

The SEC measurement results of PAN solutions in the presence of 0.075 mol/l of betaine and its absence at 298 K are listed in Table 8.

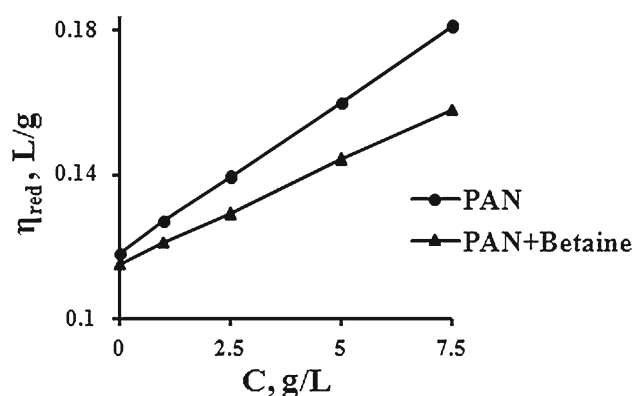


Fig. 3 Reduced viscosity dependence on concentration of the dilute solutions of PAN in the presence of 0.075 mol/L of betaine and its absence

Table 8 SEC of PAN solutions in the presence of 0.075 mol/L of betaine and its absence

Solution	PAN concentration <i>C</i> (g/L)							
	Conductivity χ ($\mu\text{S}/\text{cm}$)							
	5	10	20	30	40	60	80	100
PAN	12.3	23.0	39.1	52.8	64.0	82.6	92.1	97.5
PAN+betaine	11.0	20.1	36.3	50.1	62.0	77.1	86.1	88.6

SEC of DMF equals to 0.7 $\mu\text{S}/\text{cm}$ at 298 K

Figure 4 shows the relationship between SEC and PAN concentration in the presence of 0.075 mol/L of betaine and its absence.

Figure 4 shows that the SEC of the PAN solutions increases with PAN concentration sharply. Then, it slows down at high concentrations, where the structural association is maximal, and then the conductivity is no longer linked to the concentration in practice. Additionally, Fig. 4 shows that adding betaine to the polymeric solutions conductivity decreases 7.5 % on average at high concentrations. This happens because of intermolecular interaction between betaine

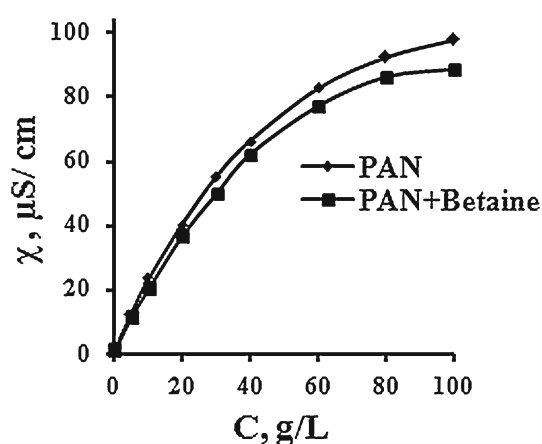


Fig. 4 SEC dependence on PAN concentration in the presence of 0.075 mol/L of betaine and its absence at 298 K

and polar groups of PAN, which leads to a decrease in the number of dipoles capable of transmitting electrical current [22–24].

Two solid samples are prepared, as described in the experimental section, the first one is PAN 100 g/L, and the second one is PAN 100 g/L containing 0.075 mol/L of betaine. Then, these samples are tested by FT/IR, XRD and SEM. Figures 5 and 6 show the infrared spectrum of two preceding solid samples.

From Fig. 5 we can find that the peak position of $\text{C} \equiv \text{N}$ group at 2247 cm^{-1} (3) belongs of acrylonitrile, $\text{C}=\text{O}$ group at 1736 cm^{-1} (4) belongs to vinylacetate and $\text{C}=\text{O}$ group at 1669 cm^{-1} (5) belongs to acrylamide. Figure 6 shows that the peak position of $\text{C} \equiv \text{N}$ group (2) belongs of acrylonitrile and $\text{C}=\text{O}$ group (3) belongs to vinylacetate with no change, while the peak position of $\text{C}=\text{O}$ group belongs to acrylamide has shifted to a lower wave number 1655 cm^{-1} (4). This finding indicates hydrogen bonding formation between the carbonyl groups of acrylamide and the amide groups in betaine. We conclude that the interactions between PAN and betaine are

Fig. 5 IR spectrum of PAN 100 g/L

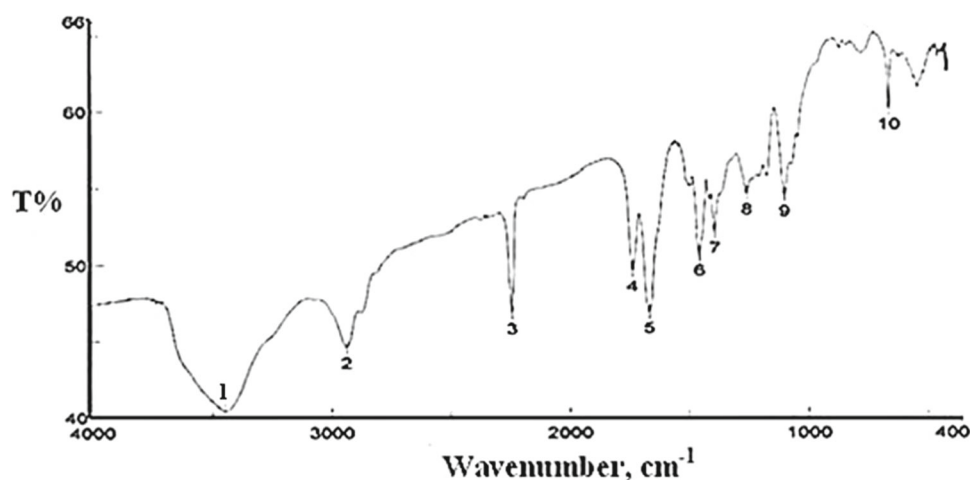


Fig. 6 IR spectrum of PAN 100 g/L containing 0.075 mol/L of betaine

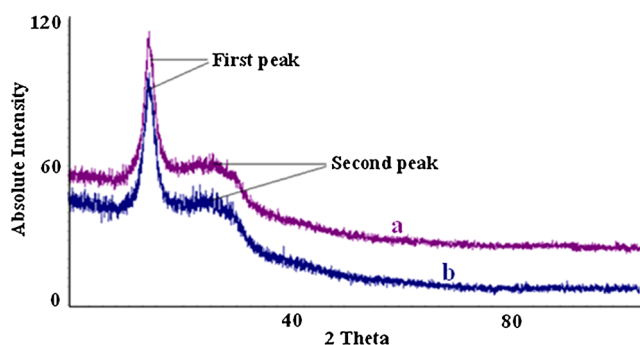
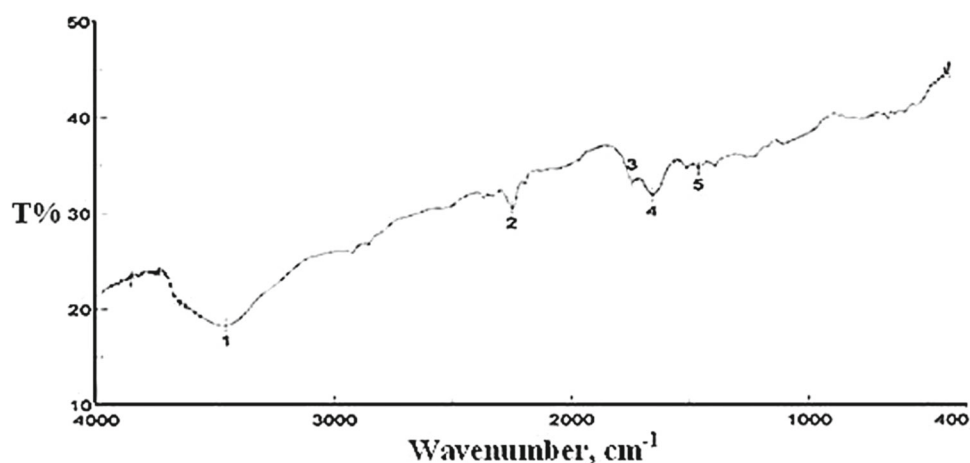


Fig. 7 X-ray diffraction patterns. (a) PAN 100 g/L containing 0.075 mol/L of betaine. (b) PAN 100 g/L

the cause of the changes in viscosity and conductivity solutions discussed previously [25–27].

The two preceding solid samples are examined by the X-ray diffractometer which has software to evaluate crystalline structure. Figure 7 shows the X-ray diffraction patterns.

Figure 7 shows that X-ray diffraction patterns have two peaks; the first one has a strong intensity, while the second is weak and broad. The first peak indicates a crystalline structure, while the second peak indicates that there is a small amount of amorphous structure [28]. From Fig. 7a, we can find that the intensity of the first peak increases slightly in comparison with the first peak in Fig. 7b which proves that the crystalline structure has developed in the presence of betaine.

Moreover, the two preceding solid samples are examined by the SEM as shown in Fig. 8.

From Fig. 8 we find that the crystalline structure of the first sample (8a) is more developed than the second sample (8b). This happens because of the existence of betaine which has worked to decrease the interfacial surface tension, and

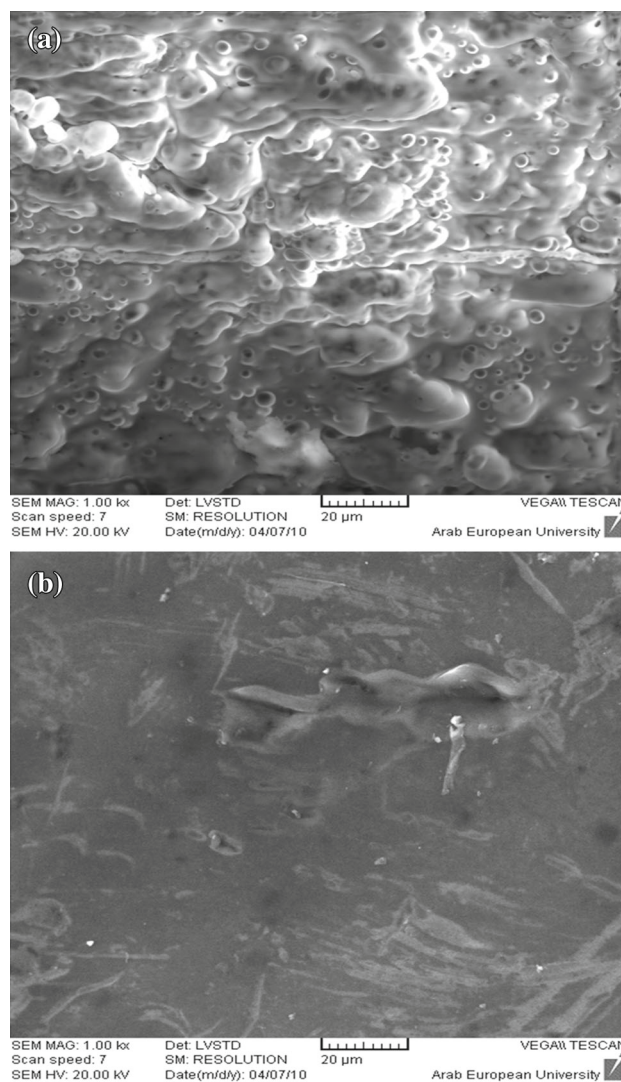


Fig. 8 Morphology of PAN. a PAN 100 g/L containing 0.075 mol/L of betaine. b PAN 100 g/L

this corresponds with what has been mentioned before in the study of structure through XRD.

4 Conclusions

Enthalpy plays a significant role in the micelle formation in DMF medium. Temperature change does not affect the mechanism of a crystalline structure formation of PAN solutions. The presence of betaine in the PAN solutions does not lead to change in the percolation threshold of a crystalline structural formation. Viscosity, conductivity and activation energy of viscous flow of PAN solutions decrease in the presence of betaine surfactant. Hydrodynamic volume of macromolecules of PAN decreases in the presence of betaine. The hydrogen bonding formation between the carbonyl groups of acrylamide in PAN and the amide groups in betaine has been confirmed by FT/IR spectra. Crystalline structure of PAN has developed in the presence of betaine. Thus, the foundations of formation and evolution of the structure of PAN in the presence of betaine have been laid.

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